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Sandia National Laboratories  
Waste Isolation Pilot Plant (WIPP)  
Test Plan TP 00-07

## **Experimental Study of WIPP Engineered Barrier MgO at Sandia National Laboratories Carlsbad Facility**

### **Task 1.3.5.4.3.1**

Rev. 2

Effective Date: 10/02/02

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WIPP:1.3.5.3.3.3:TD:QA:DPRP1:NF:Test plan for MgO, TP 00-07, Rev. 2

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## **1.0 DEFINITION OF ABBREVIATIONS AND ACRONYMS**

ASTM	American Society for Testing and Materials
BET	Brunauer, Emmett, and Teller
CCA	Compliance Certification Application
CBFO	US DOE Carlsbad Field Office
CO <sub>2</sub>	Carbon dioxide
DAS	Data acquisition system
DOE	Department of Energy
EBSD	Electron backscatter diffraction
EDS	Energy dispersive system
GC-MS	Gas chromatography mass spectrometer
GWB	Generic Weep Brine (synthetic Salado Formation brine)
HA	Humic acids
ICP-OES	Inductively-coupled plasma optical emission spectrometer
ISA	Isosaccharinic acid
LANL	Los Alamos National Laboratory
LOI	Loss on ignition
MgO	Magnesium Oxide
M&TE	Measuring and test equipment
NIST	National Institute of Standards and Technology
NBS	National Bureau of Standards
NP	Nuclear Waste Management Program Procedure
NWMP	Nuclear Waste Management Program
RWP	Radiological work permit
SEM	Scanning electron microscope
SNL	Sandia National Laboratories
SP	NWMP Activity/Project Specific Procedure
STTP	Actinide Source Term Test Program
TDIC	Total dissolved inorganic carbon

TOP	Technical operating procedure
TP	Test Plan
TRU	Transuranic
WID	Westinghouse Waste Isolation Division
WIPP	Waste Isolation Pilot Plant
XRD	X-ray diffraction

## 2.0 REVISION HISTORY

This is the second revision of this Test Plan (TP). The current revision is in response to a Corrective Action Request (CAR) # W-02-05. The previous TP did not cover hydration experiments on the engineered barrier magnesium oxide (abbreviated as MgO thereafter) nor solution chemistry of carbonation processes of the engineered barrier. More experimental details are also needed in order for a qualified technical person to sufficiently reproduce any experiment described hereafter. Descriptions of experiments concerning possible isosaccharinic acid (ISA) production, and the affect of MgO on humic acid solubilities have been removed. A separate TP will be written describing ISA experiments and subsequent analysis. The influence of MgO on the solubilities of humic acids will be described under TP 02-02, "Generation of Colloids from the WIPP Backfill".

## 3.0 PURPOSE AND SCOPE

MgO is being used in the Waste Isolation Pilot Plant (WIPP) to mitigate the effect of microbial CO<sub>2</sub> generation on actinide mobility in a post-closure repository environment (Bynum *et al.*, 1998; Papenguth *et al.*, 1998). MgO will sequester CO<sub>2</sub> and buffer brine pH at a moderately basic level, thus minimizing solubilities of actinides in WIPP brines. In the past, a series of experiments have been conducted at Sandia National Laboratories (SNL) to verify the efficacy of MgO as a chemical control agent in the WIPP (See Test Plans TP 97-01 and TP 98-05). The experimental conditions in the current revision bracket those expected in the WIPP. Therefore, the results from these experiments directly support re-certification and the Performance Assessment (PA).

With the development of a laboratory facility at the SNL Carlsbad Program Group, MgO experiments were transferred to Carlsbad and new experiments have been initiated. This Test Plan provides guidance only for the studies of MgO to be conducted at SNL-Carlsbad Laboratory. The following tasks are planned:

- *Characterization of the MgO being emplaced in the WIPP.* The purpose of this study is to analyze Premier Chemical's MgO (or any subsequent supplier) to determine what impurities might be present and in what quantities, and to describe the granular texture. Analysis is done using the JEOL 5900LV scanning electron microscope (SEM), the Brucker X-ray Diffractometer (XRD), and chemically by a gravimetric silica method (Kolthoff and Sandel, 1961). The results will influence the quantity of MgO that will be emplaced in the WIPP in order to sequester all the CO<sub>2</sub> produced from possible microbial activity, and would provide important information such as the content of CaO, which might influence the reaction path calculations.
- *Further study on the hydration of Premier Chemicals MgO.* The hydration of MgO must occur before the engineered barrier can react with CO<sub>2</sub>, which may be formed from possible microbial degradation of organic materials in the waste package. Hydration may also be the rate-limiting step to carbonate formation. These experiments are being conducted to evaluate several factors affecting MgO hydration rate under both inundated and humid conditions.

The results will help determine hydration rates and pathways, and whether the reaction solid products passivate the reactivity of MgO.

- *Further study of the kinetics of magnesium carbonate formation and conversion to magnesite under WIPP-relevant conditions.* The reaction of MgO with CO<sub>2</sub> can produce a series of magnesium carbonate minerals with magnesite (MgCO<sub>3</sub>) as the most stable phase (Königsberger *et al.*, 1999). Different magnesium carbonate and hydroxycarbonate minerals can have different buffering capabilities for controlling CO<sub>2</sub> fugacity and brine pH. In the WIPP Compliance Certification Application (CCA), it is assumed that metastable magnesium carbonate minerals will be ultimately converted to magnesite. The first objective of this task is to obtain the rates of carbonation of the engineered barrier to metastable magnesium carbonate(s). The second objective is to estimate the kinetics of the conversion of the metastable magnesium carbonate to magnesite to provide additional data to support the CCA assumption. This task will also support the US Department of Energy (DOE) Carlsbad Field Office's (CBFO's) effort to simplify the existing MgO engineered barrier system.
- *Experimental determination of iron concentrations in GWB and ERDA-6 in contact with the engineered barrier owing to metal corrosion.* The influence of corrosion of metals on the chemical environment in the WIPP has been well envisioned before by Brush (1990). Should low-carbon steel, that is used as the waste packaging material for the WIPP, corrode in brines then iron would dissolve. This may influence the brine chemistry and the solid mineral assemblage of the WIPP. Siderite (FeCO<sub>3</sub>) has lower solubility than that of magnesium carbonate(s) expected in the final assemblage of the WIPP after the closure. Therefore, the formation of siderite may also consume some of carbon dioxide generated by microbial activity and might influence the important physicochemical parameters such as pH and  $f_{\text{CO}_2}$ . The iron concentrations under buffered conditions relevant to the WIPP will support the future EQ3/EQ6 calculations and therefore the actinide solubility calculations.

## **4.0 EXPERIMENTAL PROCESS DESCRIPTION**

### **4.1 Overall Strategy and Process**

#### **4.1.1 Experimental Design**

##### ***Task 1. Characterization of the MgO being emplaced in the WIPP.***

Premier Chemicals is the vendor currently supplying MgO to the WIPP. This material is produced by calcining magnesite ore in a rotary kiln, mined at Gabbs, NV, and consists of angular grains of material  $\leq 3/8$  inch in diameter (much of the material is fine powder.) The ore bodies were hosted in Upper Triassic dolomites, which were deformed and intruded by felsic dikes and stocks. The geological origin of such ore bodies can provide additional information for the interpretation of impurities in the engineered barrier material. The material has a minimum of 90 wt.% of MgO (as stated on the Material Safety Data Sheet issued before 2000), and is relatively impure, containing up to 10 percent Mg-Ca silicates. The chemical makeup of a typical sample of Premier MgO, as listed in the Material Safety Data Sheet issued before 2000, is

as follows: 2.8 wt.% of  $\text{SiO}_2$ , 1.3 wt.% of  $\text{Fe}_2\text{O}_3$ , 0.8 wt.% of  $\text{Al}_2\text{O}_3$ , 3.9 wt.% of  $\text{CaO}$ , and 91.0 wt.% of  $\text{MgO}$  (90 % minimum). Note that the impurity oxides listed here do not exist as free oxides in the  $\text{MgO}$  (with the exception of a fraction of the  $\text{CaO}$  and  $\text{SiO}_2$ ) but are combined mineralogically as calcium-magnesium silicates, aluminates, and ferrites. As of October 2000, Premier Chemicals has adjusted the chemical composition to a minimum of 95 wt.% of  $\text{MgO}+\text{CaO}$ .

The purpose of this task was to analyze Premier Chemical's  $\text{MgO}$  to determine what impurities might be present and in what quantities, and to describe the granular texture of Premier Chemical's  $\text{MgO}$ . Physical analyses were done using the JEOL 5900LV scanning electron microscope (SEM), and the Bruker X-ray Diffraction unit (XRD). Chemical analyses were done using a gravimetric determination of silica method (Kolthoff & Sandell, 1961).

All samples are analyzed by using the SEM and the XRD. The SEM is utilized to identify major and minor mineral phases, and to document the grain textures, the physical distribution of the minerals, and the intergranular porosity.

The gravimetric determination of silica method by Kolthoff & Sandell (1961) is adopted to determine the amount of  $\text{SiO}_2$  present in the current batch of Premier Chemical's  $\text{MgO}$  being emplaced in the WIPP. Before analysis,  $\text{MgO}$  is crushed to a size of  $< 200$  mesh ( $75\ \mu\text{m}$ ).  $\text{MgO}$  is then mixed with sodium carbonate and ignited. Samples are first leached with  $\text{HCl}$ , and then placed on hotplates to evaporate overnight. Remaining solids are filtered, re-ignited, and weighed. Liquid is retained from the filtering for analysis by the Perkin Elmer inductively coupled plasma optical emission spectrometer (ICP-OES), for identification of any aluminates that might be present. From the silica results, the weight percentage of  $\text{Mg}_2\text{SiO}_4$  or  $\text{CaMgSiO}_4$  is determined.

ICP-OES (Perkin Elmer DV 3300) is used to determine the concentration of Al, Mg, Ca, and Si in liquid left from the gravimetric determination of silica. The results are used to determine whether all silicates were filtered out in the above method and if any lime and aluminates constitute certain percentages of Premier  $\text{MgO}$ .

### ***Task 2. Further study on the hydration of Premier Chemicals $\text{MgO}$***

Hydration experiments were developed to determine hydration rates and pathways, and whether the reaction solid products inhibit the reactivity by passivation of  $\text{MgO}$  under both inundated and humid conditions. These experiments will be run at fixed and variable brine/ $\text{MgO}$  ratios. Many samples will be agitated daily to eliminate the effect of mass transport, whereas others will be non-agitated to better represent WIPP relevant conditions.

#### **Inundated Experiments**

In the first set of experiments, five grams of Premier  $\text{MgO}$  is placed in 125 ml polypropylene bottles. Each bottle contains 100 ml of one of four solutions—deionized (DI) water, 4.0 M  $\text{NaCl}$ , and synthetic Salado (GWB) and Castile (ERDA-6) brines. The first two simple solutions are included in an effort to develop an understanding of the effect of the ionic strength on the hydration process. The bottles are sealed and no special effort is made to exclude



CO<sub>2</sub> from these experiments (and all other hydration experiments). CO<sub>2</sub> diffusion into the system will be insignificant relative to the hydration rate. Samples are aged in ovens at 25-90° C, and are agitated frequently. Sample agitation is performed to eliminate the formation of a cemented cake of hydration products, removing the possibility that cake formation will inhibit hydration by limiting brine access to the bulk MgO. However, hydration products may still inhibit further hydration by coating individual particles, or by plugging the internal porosity in the MgO grains. The effects of cake formation on hydration are being examined in a separate set of experiments described in detail below. Periodically, samples are removed from the ovens, cooled, and the pH measured. The solid fraction is then vacuum filtered out by using Whatman #40 filters, and rinsed with DI water to remove any remaining brine. Then the filtered solids are dried, ground, and characterized by XRD and SEM. The loss on ignition (LOI) at 500° C (brucite dehydrates at ~350°C) is used to calculate the amount of hydrated material in each sample.

To date two hydration products, magnesium hydroxide (brucite) and magnesium chloride hydroxide hydrate, have been recognized. Magnesium chloride hydroxide hydrate is present only in the GWB and continues to be formed instead of brucite until the Mg<sup>2+</sup> concentration falls below ~0.7 M. Therefore, the second set of experiments is designed to test whether relative proportions of brucite to magnesium chloride hydroxide hydrate will vary as a function of the volume of brine present. This set of experiments evaluates the effect of variable brine volumes present in GWB/MgO systems. Five grams of MgO are placed in 125 and 250 ml polypropylene bottles containing GWB volumes ranging from 60–250 ml, and aged for 28 days at 70°C. It is possible that in the future lower brine to MgO ratios may need to be investigated.

In addition, the third set of experiments is being conducted to assess the effect of brine to MgO volume ratios on the hydration rates in a manner similar to the inundated hydration experiments described above, except 2.5 times as much GWB is used in this set of experiments. The aim of this set of experiments is to compare the resulting hydration rate curves with those of the above mentioned inundated experiments. The comparison will define the effect of the brine to MgO ratios on the hydration rates. Samples are placed in the 70°C oven and are sampled at the same interval as the first inundated samples at 70°C.

#### Cemented Cake Experiments

The effects of possible formation of a cemented cake of hydration products on hydration rates are being examined. In this set of experiments, five (15 g)-, ten (30 g)-, and fifteen (45 g)-mm-thick layers of Premier MgO are placed in 125 ml polypropylene containers with 100 ml GWB or ERDA-6, and are placed in ovens at 25°–90° C. The samples are not agitated. Sampling is being carried out over weeks to months. Samples are taken from the oven, cooled, and pH is measured. Samples in their entirety are filtered, dried, and crushed, then analyzed by LOI and XRD. The SEM is used to perform cross-sectional analysis on select samples before they are crushed.

#### Humid Experiments

The humid hydration experimental runs involve uncrushed Premier MgO as starting material and are being conducted at temperatures of 25°C, 40°C, 60°C, and 80°C and relative

humidities of 35%, 50%, 75%, and 95%. These humidities bracket the expected WIPP value of 70%. Premier Chemicals MgO is contained in 6-well polycarbonate trays, with three grams of MgO in each well. Four trays are stacked in sealed polypropylene containers. Each container contains a saturated salt solution providing the desired relative humidity (Table 1). Relative humidity will vary a few percent with temperature, exception being NaBr · 2H<sub>2</sub>O. Currently, the humidity change with temperature is being investigated.

Table 1. Saturated Salt Solutions and the Relative Humidity Values they Produce.

Salt Solutions	RH Value, %*
K <sub>2</sub> SO <sub>4</sub>	96
NaCl	75
NaBr	53
MgCl <sub>2</sub>	33

\* RH values vary a few % with temperature

The trays in each container are elevated above the salt solution on plastic blocks. Holes have been drilled in the bottom and top of each tray; and the upper lip of each well is notched. The holes and notches allow for circulation through each sample well. This set of experiments consists of 384 samples (four temperatures, four relative humidities, four trays, six wells per tray).

Samples will be periodically collected over a period of months to years depending on reaction rates. Each sample is dried and analyzed by LOI and XRD. The fraction of brucite will be determined by weight loss at 500°C. This technique assumes that brucite is the only reaction product of hydration of MgO. A few samples will be analyzed by XRD to verify that carbonate formation is not significant under humid conditions.

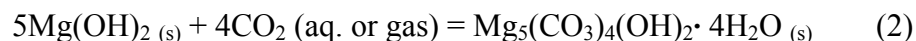
### ***Task 3. Further study of the kinetics of Mg carbonate formation and conversion***

Reaction of MgO with CO<sub>2</sub> can produce a series of magnesium carbonate minerals with magnesite as the most stable phase (Königsberger et al., 1999). Different magnesium carbonates impose different values of CO<sub>2</sub> fugacity and brine pH. The objectives of current experiments in this task are to gain a more mechanistic understanding of MgO carbonation processes and determine which magnesium carbonate phase will eventually control the  $f_{\text{CO}_2}$ . These experiments will help determine: (1) how solution chemistry affects magnesium carbonate formation; which in turn will control brine  $f_{\text{CO}_2}$  and possibly pH; (2) the carbonation rates of Premier Chemicals MgO and brucite under various conditions. MgO is expected to first hydrate as brucite, and is expressed by Eq. (1),



and hydration rates can be obtained from hydration experiments described in detail above, the experiments planned here will focus on the formation of magnesium carbonate minerals from

the reaction of brucite with CO<sub>2</sub> to determine the carbonation rates. Using hydromagnesite as an example, the carbonation of brucite can be expressed as the following reaction,



However, in order to investigate the overall carbonation rates from MgO to magnesium carbonate(s), additional experiments will be conducted using MgO as a starting material, which may correspond to the combination of reactions (1) and (2). As suggested by reaction (2), the carbonation can take place in both aqueous (inundated) and gaseous (humid) media. Hence, experiments will be designed to investigate the carbonation rates in both scenarios, which will be described in detail below.

Brucite will be purchased or synthesized using Premier MgO backfill. (Brucite crystals will be crushed into fine-grained powder, and the specific surface area of brucite powders will be determined using the B.E.T. (Brunauer, Emmett, and Teller) autocontrol physical adsorbent instrument (ASAP2000) (Wang et al., 1999).

#### Experiments Using MgO as Starting Material

The first set of carbonation rate experiments are run at two different partial pressures of CO<sub>2</sub>, under atmospheric conditions ( $3\text{--}4 \times 10^{-4}$  atm) and 5% CO<sub>2</sub> ( $5 \times 10^{-2}$  atm). In the future experiments may be run under other partial pressures, such as 1/10<sup>th</sup> atmospheric CO<sub>2</sub>.

The experiment running under atmospheric P<sub>CO<sub>2</sub></sub> conditions are using four different solutions: DI water, 4 M NaCl, GWB, and ERDA-6. Each 125 ml polypropylene sample bottle includes five grams Premier Chemicals MgO and 100 ml of solution. Room air is bubbled continuously through the samples using a gas manifold. Each manifold holds 24 samples. To minimize evaporation, the air is humidified by bubbling through water prior to entering the manifold.

Samples are collected at weekly intervals and eventually will be collected on a monthly to bimonthly interval. Samples are measured for pH, filtered, dried, and crushed. The amounts of carbon incorporated into the reaction products are determined by using a UIC Inc. carbon coulometer and carbonate phases will be identified by using XRD. Based on the amounts of carbon incorporated into the reaction products, carbonate conversion rates will be assessed. New sets of samples will be added to the experiment periodically to extend the curve.

The experiments with 5% CO<sub>2</sub> will quantify carbonation rates in two brines, GWB and ERDA-6. There are 64 samples (two brines, four solids, eight samples). Each polypropylene bottle contains five grams of one of the following solids: Premier Chemicals MgO, Fisher Scientific MgO, pre-hydrated, crushed Premier Chemicals MgO, and pre-hydrated Fisher MgO. Hydrated samples are prepared by adding five grams of either crushed Premier Chemicals MgO, or Fisher MgO to 100 ml of brine. The bottles are placed in a 90°C oven for approximately three to four weeks. Before the pre-hydrated samples are added to the manifold, a small portion is sampled and will be analyzed for brucite. The experiments with 5% CO<sub>2</sub> will be sampled at a

higher frequency due to the anticipated accelerated reactions. New sets of samples will be added to the experiment periodically to extend the curve.

All samples in the experimental set using 5% CO<sub>2</sub> are placed in a glovebox with a controlled atmosphere. The five percent of CO<sub>2</sub> is controlled by delivering a mixture of 95% N<sub>2</sub> and 5% CO<sub>2</sub> into the glovebox at a fixed rate. To bring the atmosphere of the glovebox up to 5% CO<sub>2</sub> in a timely manner after the box is opened for sampling, dilute sulfuric acid is mixed with sodium bicarbonate within the glovebox, which releases a pre-determined amount of CO<sub>2</sub> to the atmosphere.

#### Experiments Using Brucite as Starting Material

The objectives of experiments using brucite as starting material are two-fold: (1) to determine precisely the carbonation rates, and at the same time (2) to monitor the solution chemistry in order to document the progress in carbonation processes. The second objective is mainly due to the fact that the assemblage of brucite and magnesium carbonate(s) resulting from the carbonation would influence the solution chemistry (Stumm and Morgan, 1996). While the results from the first objective would provide the firm basis for the performance assessment for the conceptual model of the WIPP, the results from the second objective would provide an important insight into (1) the reaction path when solution are in contact with brucite, (2) the identity of the solid phase that controls the solubility in terms of Mg concentrations, and (3) whether important physicochemical parameters such as pH are buffered by the assemblage of brucite and its carbonation product(s) (i.e., hydromagnesite).

In the first set of experiments, brucite powder will be added to various solutions and allowed to react with the dissolved CO<sub>2</sub> at fixed P<sub>CO<sub>2</sub></sub> in polyethylene bottles and 25 mL glass vials. The volume of polyethylene bottles ranges from 25 to 1000 mL. The weight of brucite associated with experimental runs using polyethylene bottles ranges from 1.5 grams to 15 grams, and the volume of solutions employed is in the range from 25 to 1000 mL. In experimental runs using 25 mL glass vials, the weight of brucite ranges from about 1.2 grams to 2.5 grams, whereas the weight of solutions ranges from 17 grams to 25 grams. In this set of experiments, several P<sub>CO<sub>2</sub></sub> will be employed, including  $3\text{--}4 \times 10^{-4}$  atm (atmospheric CO<sub>2</sub>). In such atmospheric CO<sub>2</sub> experiments, caps of polyethylene bottles and glass vials are not closed in order to allow solutions to communicate with atmospheric CO<sub>2</sub>. DI water, and brines expected to be present at the WIPP such as GWB and ERDA-6 (Brush, 1990; Zhang *et al.*, 1999) will be used. To assess the effect of ionic strength on the carbonation rates, four solutions with different ionic strengths (0.01 M, 0.1 M, 1.0 M and 4.0 M NaCl solution) will be used. In most of the above experiments, solutions and starting materials will not be stirred, and such experiments are termed “static runs”. In order to assess the effect of mass transport on carbonation rates, a subset of experiments will be conducted under the same conditions, but solutions and starting materials are continuously stirred and compressed air continuously bubbles into solutions, and such experiments are termed “dynamic runs”. The results from both “static runs” and “dynamic runs” will be compared to evaluate the effect of mass transport on carbonation rates. During the experiments, an appropriate number of brine samples will be taken for the analysis of pH and Mg concentration in order to monitor changes in solution chemistry due to carbonation. Solutions will be sampled weekly. The mass of samples taken each time will be recorded. The mass of samples withdrawn

will be between 3 and 4.5 grams. Solution samples will be acidified with concentrated  $\text{HNO}_3$  and then be diluted to 10 mL. To disturb the steady state on purpose, each experimental run will be recharged after three or four samplings with fresh matrix solutions with approximately the same amounts that have been withdrawn. In the following sampling(s), the observations of the lack of deviations in solution chemistry after recharging from the previous samplings would imply the re-equilibration. This technique has been demonstrated before (e.g., Xiong and Wood, 2001). After sufficient time (perhaps months), the solids in each bottle will be filtered, and the resulting mineral phases will be identified using Scanning Electron Microscopy (SEM) and the associated Energy Dispersive System (EDS) and Electron Backscatter Diffraction (EBSD). EBSD is able to obtain electron diffraction patterns on a scale of  $<1 \mu\text{m}$  and therefore provides a better mineral identification capability than the X-Ray Diffraction (XRD) technique used in the previous MgO work (TP 96-01 and TP 98-05). The contents of carbonates in solid phases will be analyzed by using a  $\text{CO}_2$  coulometer (UIC, Inc., Model CM5014). The majority of carbonation experiments will be conducted at room temperature. Additional experiments will be conducted at  $40^\circ\text{C}$ ,  $50^\circ\text{C}$ ,  $60^\circ\text{C}$ ,  $70^\circ\text{C}$ ,  $80^\circ\text{C}$ , and  $90^\circ\text{C}$  in a manner similar to hydration experiments at these temperatures, which has been described in detail above.

To assess carbonation rates at lower  $\text{CO}_2$  concentrations, some experiments will be set-up to allow dissolved  $\text{CO}_2$  to diffuse into polyethylene bottles in which brucite powder is in contact with various solutions. In such diffusion experiments, caps of 250 mL polyethylene bottles will be sealed with parafilm. The weight of brucite used in such experiments will range from 4 to 6 grams, and the weight of the solutions will be from 100 to 250 grams. The sealed polyethylene bottles that contain brucite and solutions will be placed into 16 oz plastic jars filled with DI water. As the diffusivity of  $\text{CO}_2$  through polyethylene has been established (Dietzel and Usdowski, 1996), the flux of  $\text{CO}_2$  into polyethylene bottles by diffusion will be precisely calculated. The diffusion of  $\text{CO}_2$  through polyethylene is expressed as:

$$\frac{dN}{dt} = FD \frac{C_s - C}{\Delta X} \quad (3)$$

where  $N$  is the number of moles,  $F$  is the surface area of diffusion,  $D$  is the diffusion coefficient of  $\text{CO}_2$ ,  $C_s$  and  $C$  are the concentrations of dissolved  $\text{CO}_2$  in the jar and the polyethylene bottle, respectively, and  $\Delta X$  is the thickness of the polyethylene. The total diffusion surface of the 250 mL polyethylene bottle is  $\sim 300 \text{ cm}^2$ , and the thickness of the bottle is 0.2 cm. Assuming that the pressure of  $\text{CO}_2$  delivered to the jar is 1 atm and substituting  $D_{\text{CO}_2} = 10^{-7.9} \text{ mole cm}^{-2}$  (Dietzel and Usdowski, 1996) into Eq. (3), the flux can be calculated to be  $\sim 8 \times 10^{-10} \text{ mole s}^{-1}$ . As the initial concentration of Mg in the polyethylene bottle is about  $10^{-3} \text{ m}$  controlled by brucite, the carbonate concentration required for the saturation of hydromagnesite is about  $10^{-4} \text{ m}$ . Therefore, it requires about one day for the dissolved  $\text{CO}_2$  to diffuse into the polyethylene bottle to reach the saturation of hydromagnesite. In the actual experiments, the pressure that will be employed will be less than 1 atm, and the experiments will be conducted in a glove box. The desired pressure of  $\text{CO}_2$  will be delivered to the glove box via a regulator. As soon as the saturation limit of hydromagnesite is reached, the fugacity of  $\text{CO}_2$  inside the polyethylene bottle will be fixed by the formation of hydromagnesite, which is  $10^{-5.14}$  bars according to the compilation of Stumm and Morgan (1996). Two temperatures, room temperature and  $40^\circ\text{C}$ ,

which bracket the expected temperature range in the WIPP, will be employed in these experiments.

In the second set of experiments, in order to evaluate carbonation rates under conditions where aqueous media are absent, brucite powder will be allowed to react with gaseous  $\text{CO}_2$  at various desired humidities. In this set of experiments, 100 mL beakers that contain about 4–6 grams of brucite will be placed into 16 oz plastic jars with lids filled with various saturated solutions. The saturated solutions include  $\text{K}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NaBr}$ , and  $\text{MgCl}_2$  solutions. These saturated solutions provide relative humidities ranging from 95% to 33% (Lide, 1997, p. 15-24 to 15-25, and references therein). These saturated solutions will be prepared according to their saturated solubilities tabulated in Lide (1997, p. 8-98 to 8-105). The lids of the jars will be opened daily to allow atmospheric  $\text{CO}_2$  to be replenished. In this set of experiments, the carbonation rates are expected to be very slow at room temperature. Therefore, in addition to experimental runs at  $25^\circ\text{C}$ , there will be also experimental runs at other temperatures ranging from  $40^\circ\text{C}$  to  $90^\circ\text{C}$ . These experimental runs at higher temperatures would allow extrapolations of carbonation rates under humid conditions to room temperature with confidence. For the purpose of comparison, the lids of some jars will not be opened until the termination of the experimental runs. Such comparison might provide an understanding of the carbonation rate at low  $P_{\text{CO}_2}$  as  $\text{CO}_2$  in the experiments in which the lids will not be opened daily would rely on the diffusion of atmospheric  $\text{CO}_2$  into the jars.

In the third set of experiments, the metastable Mg carbonate mineral phases will be incubated in various solutions at  $25^\circ\text{C}$ . Thermodynamically, magnesite ( $\text{MgCO}_3$ ) is the stable phase for magnesium carbonates although its crystallization at room temperature is not kinetically favored. All other magnesium carbonates are considered as metastable phases. The metastable magnesium carbonate phases used in this set of experiments will be purchased from Ward's Natural Science Establishment (Rochester, NY) and Excalibur Mineral Company. Two major metastable phases of magnesium carbonate, hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) and nesquehonite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ), will be used. It has been demonstrated that metastable magnesium carbonates attain solubility equilibrium from the direction of undersaturation in a few days (e.g., Königsberger et al., 1992). Therefore, experimental runs will be monitored to reach solubility equilibrium from the direction of undersaturation, and solutions will be sampled periodically (bi-weekly). The metastable magnesium carbonates will be loaded in silver capsules, and then both ends of silver capsules will be crimped. This loading technique offers two advantages: (1) to prevent the solid starting material from being sampled while the capsule allows the starting material to communicate with solutions, and (2) to allow the experimental run products to be collected easily, especially when the amounts of the starting material are small, for other work such as XRD and SEM after the termination of the experimental runs. This loading technique has been successfully employed before (i.e., Xiong and Wood, 2001, and references therein). The mass of metastable magnesium carbonates will range from 0.1 grams to 0.5 grams, and the mass of solutions will be in the range from 20 grams to 35 grams. Solutions and silver capsules containing metastable magnesium carbonates will be in 35 mL plastic bottles. Caps of plastic bottles will not be closed to allow solutions to communicate with atmospheric  $\text{CO}_2$ . In order to keep the ionic strength constant and to compensate for the possible loss of

water in salt solutions, the experimental runs will be periodically monitored for possible loss of water by comparison with the original weight. If there is a loss of water, the exact amount of water will be added. These bottles will then be placed on a shaker at a constant shaking rate. These samples will be analyzed for Mg concentrations. This information will aid in interpreting which Mg carbonate phase might control the solubility in hydration experiments and carbonate rate experiments in aqueous media as mentioned before. As GWB and ERDA-6 have high matrix concentrations of Mg, in order to determine precisely concentrations of Mg resulting from the dissolution of the solubility-controlling phase, only DI water and NaCl solutions with different ionic strengths will be used in these experiments. The conversion from metastable magnesium carbonates to magnesite will be evaluated from two lines of evidence. First, the onset of the conversion will be deduced from solution chemistry by conducting EQ3/6 modeling (Wolery, 1992; Wolery and Daveler, 1992). This reasoning is based on the fact that the solubility of magnesite is orders of magnitude lower than that of metastable magnesium carbonates. If the modeling indicates the undersaturation with respect to metastable magnesium carbonate beyond the uncertainty of the thermodynamic data base, such undersaturation would imply that the conversion to magnesite is taking place. The second line of evidence will be from XRD analysis of the reaction solid product.

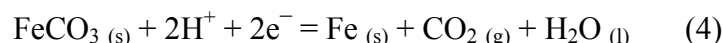
***Task 4. Experimental determination of iron concentrations in GWB and ERDA-6 in contact with the engineered barrier owing to metal corrosion***

The influence of the corrosion of metals on the chemical environment in the WIPP has been described before (Brush, 1990). The objective of this activity is to support the future EQ3/EQ6 and therefore the actinide solubility calculations. As the expected iron inventory in the WIPP is significant, the dissolved iron concentrations may influence the brine chemistry and the solid mineral assemblage of the WIPP. Siderite ( $\text{FeCO}_3$ ) has lower solubility than that of the magnesium carbonate(s) expected in the final assemblage of the WIPP after the closure. Therefore, in addition to the engineered barrier, the precipitation of siderite may also consume some of carbon dioxide generated by microbial activity and influence the important physicochemical parameters such as pH and  $f_{\text{CO}_2}$ . It is anticipated that siderite would appear in the early stage after the closure of the WIPP if the dissolved iron concentrations reaches the level dictated by the solubility of siderite, as secondary siderite has been observed in current mine tailings (Al *et al.*, 1997).

Previous experimental studies subcontracted to Pacific Northwest National Laboratory (PNNL) determined the corrosion rate of steel (Telander and Westerman, 1993, 1997). Although they reported iron concentrations for two types of experiments (anoxic-brine seal-welded-container and brine/ $\text{CO}_2$  seal-welded-container tests) which ranged from less than 10 mg/L to 1480 mg/L (Telander and Westerman, 1993), such chemical data cannot be used for modeling purposes based on the following facts. First, these corrosion experiments were not buffered with respect to pH dictated by the engineered barrier material (MgO) and to oxidation potentials (Eh) that may be expected at the WIPP. For example, in their brine/ $\text{CO}_2$  seal-welded-container tests, pH varied from 3.4 to 7.3, far from the pH values expected in the WIPP (pH = 9–10). Although the expected oxidation potentials at the WIPP are not well constrained, it is likely to be buffered by the certain assemblages such as Fe- $\text{FeCO}_3$  (Brush, 1990). If it is buffered by this assemblage,

the expected  $Eh$  would be  $-0.62$  volts at  $pH$  10 assuming  $\log f_{CO_2}$  is  $-5$  bars. Second, when their solutions in anoxic-brine seal-welded-container testes were exposed to air prior to analysis, dissolved iron was precipitated from the solution because of the oxidation. No attempt was made to re-dissolve these precipitates. Therefore, their analyses for anoxic seal-welded-container tests significantly underestimated real iron concentrations in brines. In the follow-up corrosion experiments using ERDA-6 and GSEEP brines at PNNL (Wang et al., 2001), iron concentrations in the brines were not determined or reported.

In this study, low-carbon steel (the waste packaging material for the WIPP) will be incubated in GWB and ERDA-6 brines with Premier Chemicals MgO and pre-hydrated Premier Chemicals MgO. The weight ratio of brine to MgO will range from 0.5 to 0.8 as expected at the WIPP according to the calculations by Larry Brush (2002). The  $pH$  will be dictated by the reaction of MgO with brines. Oxygen fugacity will be buffered by various solid assemblages including the Fe-FeCO<sub>3</sub>, Fe-Fe(OH)<sub>2</sub>, and Zn-ZnO assemblages. Using Fe-FeCO<sub>3</sub> as an example, the half-cell reaction can be expressed as follows (Anderson and Crerar, 1993),



Assuming unity for the activity of iron, siderite and water, oxidation potentials,  $Eh$ , for Reaction (4) can be expressed as:

$$Eh = E^\circ - \frac{2.303RT}{2F} \log f_{CO_2} - \frac{2.303RT}{F} pH \quad (5)$$

Where  $F$  is Faraday constant ( $96485.3 \text{ C mol}^{-1}$ ),  $R$  is ideal gas constant.  $E^\circ$  is given by

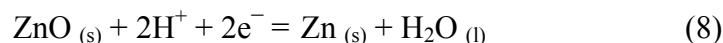
$$\Delta G_r^\circ = -2 F E^\circ \quad (6)$$

According to the compilation of Stumm and Morgan (1996),  $\Delta G_{f, \text{siderite}} = -666.7 \text{ kJ mol}^{-1}$ ,  $\Delta G_{f, CO_2, \text{gas}} = -394.37 \text{ kJ mol}^{-1}$  and  $\Delta G_{f, H_2O, \text{liquid}} = -237.18 \text{ kJ mol}^{-1}$  at reference state ( $25^\circ\text{C}$  and 1 bar), the free energy for Reaction (4) is  $35.15 \text{ kJ mole}^{-1}$ . Assuming  $\log f_{CO_2}$  is  $-5$ , therefore, we have

$$Eh = -0.0325 - 0.059 pH \quad (7)$$

The relation between  $Eh$  and  $pH$  is plotted in Figure 1.

Similarly, for the Zn-ZnO assemblage, we have



In a manner similar to the above Fe-FeCO<sub>3</sub> assemblage and using  $\Delta G_{f, ZnO} = -76.028 \text{ kcal mol}^{-1}$  at reference state from Stumm and Morgan (1996),

$$Eh = -0.42 - 0.059 pH \quad (9)$$



According to Eq. (9), the Zn-ZnO assemblage would provide an oxidation potential of -1.01 volts at 25°C. This assemblage has been observed to equilibrate fast and to buffer oxidation potentials in a few days (Nguyen-Trung et al., 1997). The dissolution of under the Zn-ZnO buffer would provide the lower limit of the iron concentrations. Low-carbon steel, Premier MgO or pre-hydrated Premier MgO, the oxygen fugacity buffer assemblage and brines will be placed into 250 mL plastic bottles, and then caps of plastic bottles will be well sealed with parafilm. Low-carbon steel will be used in the majority of experiments. For the sake of simplicity, pure iron will be employed in some experiments. The bottles containing the above-mentioned starting materials and brines will be placed in a glove box under N<sub>2</sub> atmosphere. For comparison, some experimental runs will use Premier MgO and other experimental runs will use pre-hydrated Premier MgO. A series of such experimental runs will be conducted. They will be terminated at various time scales (probably monthly). After termination of the experimental run, the solution will be filtered and be acidified with concentrated HCl, and then will be promptly analyzed using ICP-OES for Fe, Mg, Zn and other minor metals which low-carbon steel may contain by. Solid samples will be washed with DI water and dried for XRD studies.

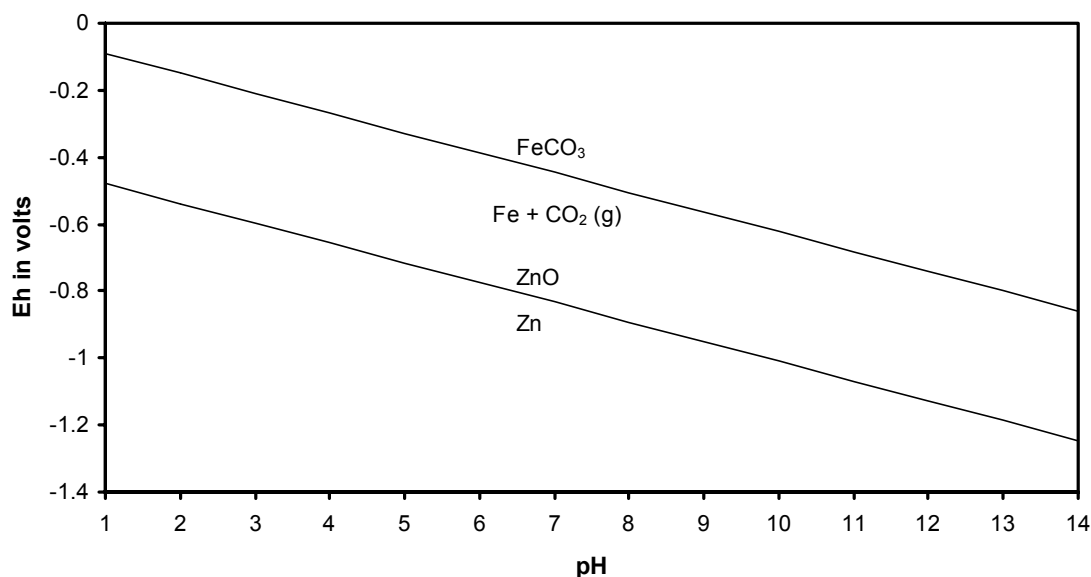


Figure 1 Oxidation potentials provided by the assemblages of Fe-FeCO<sub>3</sub> and Zn-ZnO.

#### 4.1.2 Brine Composition

Synthetic WIPP brines are used in all the experiments except those run under humid conditions. ERDA-6 is a saturated brine that contains mainly NaCl along with minor amounts of other solutes and represents fluids from reservoirs in the Castile Formation. ERDA-6 has 4.85 M of sodium, 4.64 M of chloride, and 167 mM of sulfate. GWB is a saturated brine with 3.54 M of sodium, 1.02 M of magnesium, 467 mM of potassium, 5.61 M of chloride, and 178 mM of

sulfate, and represents intergranular brines from the Salado Formation at or near the stratigraphic horizon of the repository.

Synthetic WIPP brines are mixed following the technical operating procedure described by Robinson (1996). Brine formulas are shown below in Table 2. The ERDA-6 brine composition is from Villarreal et al. (2000). The GWB is from Zhang et al. (1999).

Table 2. Brine Formulas for Synthetic ERDA-6 and GWB.

Composition of ERDA-6

COMPOUND	GRAMS/LITER	GRAMS/10 LITERS
MgCl <sub>2</sub> · 6H <sub>2</sub> O	3.86	38.6
NaCl	261.64	2616.4
KCl	7.23	72.3
Na <sub>2</sub> SO <sub>4</sub>	23.70	237
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O	6.00	60
CaCl <sub>2</sub> · 2H <sub>2</sub> O	1.76	17.62
NaBr	1.13	11.3

Table 2. (cont.) Brine Formulas for Synthetic ERDA-6 and GWB. Composition of GWB

COMPOUND	GRAMS/LITER	GRAMS/10 LITERS
MgCl · 6H <sub>2</sub> O	207.05	2070.5
NaCl	179.61	1796.1
KCl	34.84	348.4
Na <sub>2</sub> SO <sub>4</sub>	25.23	252.3
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O	15.06	150.6
CaCl <sub>2</sub> · 2H <sub>2</sub> O	2.03	20.3
NaBr	2.74	27.4
LiCl	0.19	1.86

## 4.2 Sample Control

The sample control for the work under this Test Plan will follow WIPP Nuclear Waste Management Program (NWMP) Procedure NP 13-1. Each sample will be appropriately labeled. Sample preparation, utilization, and final disposition will be documented in scientific notebooks. When samples are not in the possession of individuals designated as responsible for their custody, they shall be stored in a secure area with associated documentation (Chain of Custody).

### **4.3 Data Quality Control**

#### ***4.3.1 Measuring and Test Equipment (M&TE)***

A calibration program will be implemented for the work described in this test plan in accordance with NP 12-1, "Control of Measuring and Test Equipment." This M&TE calibration program will meet the requirements in NWMP procedure NP 12-1 for: (1) receiving and testing M&TE; (2) technical operating procedures for M&TE; (3) the traceability of standards to nationally recognized standards such as those from the National Institute of Standards and Technology; (4) maintaining calibration records. In addition, NP 13-1 and SP 13-1 identify requirements and appropriate forms for documenting and tracking sample possession. The spread sheet and other computer based data handling will follow NP 9-1.

#### ***4.3.2 Data Acquisition Plan***

Data collection procedures are specific to individual instruments. For details of the data acquisition for a particular instrument, see the Specific Procedures (SP) or Users Manual for that instrument. Any data acquired by a data acquisition system (DAS) will be attached directly to the Scientific Notebook or compiled in separate loose leaf binders with identifying labels to allow cross reference to the appropriate Scientific Notebook. If the instrument allows data to be recorded electronically, copies of the data disks will be submitted to the NWMP Records Center according to NWMP procedure NP 17-1 "Records." If possible, data files may be transferred to ZIP disks or CD ROM for submittal to the records center. For instruments that do not have direct data printout, the instrument readings will be recorded directly into the scientific notebook. Current versions of the DAS software will be included in the SNL WIPP Baseline Software List, as appropriate.

Quality control of the Scientific Notebooks will be established by procedures described in NWMP procedure NP 20-2 "Scientific Notebooks." Methods for justification, evaluation, approval, and documentation of deviation from test standards and establishment of special prepared test procedures will be documented in the Scientific Notebooks. Procedures including use of replicates, spikes, split samples, control charts, blanks and reagent controls will be determined during the development of experimental techniques.

The numerical data will be transferred from data printouts and scientific notebooks to Microsoft Excel (Office 97 version or later) spreadsheets. Data transfer and reduction shall be performed in such a way to ensure that data transfer is accurate, that no information is lost in the transfer, and that the input is completely recoverable. Data transfer and reduction shall be controlled to permit independent reproducibility by another qualified individual. A copy of each spreadsheet will be taped into the scientific notebook, and a second person will compare the data recorded in the notebook and that on the spreadsheet to verify that no transcription errors have occurred during technical and/or QA review of the notebook. This verification will be documented in the notebook when it is "signed off" by the reviewer.

### **4.3.3 Data Identification and Use**

All calculations performed as part of the activities of TP 00-07 will be documented in a scientific notebook. The notebook will be technically reviewed periodically by a second person, who will note concurrence by co-signing the examined material. If a discrepancy is found, that discrepancy and its resolution will be documented in the notebook. In addition, there will be periodic quality assurance reviews of the notebook to ensure that the requirements of NWMP procedure NP 20-2, "Scientific Notebooks" are addressed.

## **4.4 Equipment**

A variety of measuring and analytical equipment will be used for the work described in this test plan. This equipment includes that listed below, as well as equipment not yet purchased. A complete equipment list, including serial numbers, will be maintained in the scientific notebook. Much of the instrumentation to be used for this project is newly purchased, and operating procedures have not yet been developed or written. Scientific notebooks will be used to record all laboratory work activities.

### **4.4.1 Weighing Equipment**

Several balances are present in the facility and may be used for this project. These include a Mettler AT-261 five-decimal place electronic balance, an ANC three-decimal place balance, and top loading balances and scales with maximum ranges of 2 to 30 kilograms. Balance calibration checks will be performed routinely using the following NBS-traceable weight sets, which, in turn, are calibrated by the SNL Calibration Laboratory every 3 years:

- Troemner Calibration weight set, ASTM Class 1, Serial number 22803, 1 mg – 100 g, calibration expires 12/16/02.
- *Troemner Calibration weight*, NBS-Class 1, Serial number 42795, 100 g, calibration expires 11/19/02.
- *Troemner Calibration weight*, NBS-Class 1, Serial number 42797, 100 g, calibration expires 11/19/02.
- *Troemner Calibration weight*, NBS-Class 1, Serial number 42799, 100 g, calibration expires 11/19/01.
- *Troemner Calibration weight*, NBS-Class 1, Serial number 42800, 100 g, calibration expires 11/19/01.
- *Troemner Calibration weight*, ASTM-Class 1, Serial number 47824, 200 g, calibration expires 11/19/02.
- *Troemner Calibration weight*, ASTM-Class 1, Serial number 55335, 1000 g, calibration expires 11/19/02.
- *Troemner Calibration weight*, ASTM-Class 2, Serial number I-12, 10 kg, calibration expires 12/17/02.

Balance accuracy and precision will be checked daily or prior to use (whichever is less frequent), using the calibration weight sets listed above. Calibration checks will be recorded in the scientific notebook.

#### **4.4.2 Liquid Measuring Equipment**

Standard Laboratory Class A glassware (pipettes, volumetric flasks, etc.) will be used at all times. In addition, several adjustable Eppendorf pipettes are available for use in the laboratory. The calibration of pipettes will be checked routinely against a calibrated balance, and will be recorded in the scientific notebook.

#### **4.4.3 Other Analytical Equipment**

- *Ovens and Furnace*- Six Precision Telco Lab ovens are being used to hold samples at elevated temperatures. Temperature is monitored, maintained, and recorded on a weekly to biweekly schedule. A Fisher Isotemp furnace is used to determine LOI.
- *pH Meters and Autotitrators* – Solution pH may be measured using pH meters and/or autotitrators. A *Mettler Model MA235 pH/Ion Analyzer* and a *Mettler Model DL25 Autotitrator* will be used for this purpose. The range for all pH meters is 0.00 to 14.00. Electrodes will be calibrated before each use or daily (whichever is less frequent) with pH 4, 7, and 10 buffers manufactured by Fisher Scientific with unique lot numbers and expiration dates; traceable to the National Institute of Standards and Technology (NIST). The accuracy of the buffers is  $\pm 0.01$  pH units; buffer values will be adjusted for laboratory temperatures as per buffer instruction sheets if necessary. Calibration checks will be recorded in the scientific notebook. Measuring pH in concentrated brines is difficult, and a procedure will be developed to calibrate pH meters.
- *Equipment for Chemical Analysis* – Three instruments may be used for chemical analyses. The first is a Perkin Elmer Optima 3300 DV Inductively-Coupled Plasma Optical Emission Spectrometer (ICP-OES); the second is a Cary 300 UV-Visible Spectrophotometer; and the third, is a UIC, Inc. Carbon Analyzer, consisting of an acidification module, a furnace module, and a CO<sub>2</sub> coulometer. These instruments will be user-calibrated each time they are used and documented in the scientific notebook.
- *Equipment for Mineralogical, and Textural Characterization* – The mineralogy and texture may be characterized using either an Olympus BX60 Polarizing Microscope or a JEOL JSM 5900LV scanning electron microscope (SEM). Calibration standards will be used to verify instrument magnification when these instruments are used. Bulk sample mineralogy will be determined using a Bruker AXS D-8 Advance X-Ray Diffractometer (XRD). A mineral standard will be run periodically to verify diffraction line positions. Calibration results will be documented in the scientific notebook.

NMWP Activity/Project Specific Procedures (SPs) will be written for these instruments as necessary. Until that time, detailed procedure descriptions will be documented in laboratory notebooks.

## **5.0 Training**

All personnel involved in the experiments described in this Test Plan will be trained and qualified for their assigned work. This requirement will be implemented through NWMP procedure NP 2-1, “Qualification and Training.” Evidence of training to assigned NPs, SPs, TOPs, TP 00-07, ES&H procedures, and any other required training will be documented through Form NP 2-1-1 *Qualification and Training*. Annual Refresher QA training will ensure on-site personnel are trained to the NWMP QA Program. Specifically, the following Nuclear Waste Management Program Procedures (NPs) and Activity/Project Specific Procedures (SPs) are applicable:

- SOP-C001 – “Standard Operating Procedure for Activities in the SNL/Carlsbad Laboratory Facility.”
- SP 13-1 – “Chain of Custody”
- NP 6-1 – “Document Review Process”
- NP 13-1 – “Sample Control”
- NP 12-1 – “Control Of Measuring And Test Equipment”
- NP 20-2 – “Scientific Notebooks”
- NP 2-1 – “Qualification and Training”
- NP 17-1 – “Records”

In addition, SPs will be written for use of the ICP, SEM, XRD, Carbon analyzer, UV-Vis spectrophotometer, and assorted balances and scales used in the laboratory. Sample preparation procedures, which may vary from sample to sample as work scope evolves, will be detailed in Scientific Notebooks, in accordance with NWMP procedure NP 20-2.

## **6.0 Health and Safety**

All of the health and safety requirements relevant to the work described in This Test Plan and the procedures that will be used to satisfy these requirements are described in ES&H standard operating procedures. SOP-C001 describes the non-radiological hazards associated with these experiments and describes the procedures to deal with those hazards, including all the training requirements for personnel involved in conducting the experiments. In addition, a Radiological Work Permit (RWP) will be written for procedures involving use of the X-Ray Diffractometer. Additional SPs and RWPs may be mandated by SNL ES&H requirements and their issuance will not require revision of this Test Plan.

## **7.0 Permitting/Licensing**

There are no special licenses or permit requirements for the work described in this Test Plan.

## 8.0 References

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